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DIRECT DETERMINATION OF γ′ / γ′+γ / γ PHASE BOUNDARIES IN Ni-Al-Cr SYSTEM BASED ON ENTHALPY OF FORMATION RESULTS OBTAINED BY CALORIMETRIC SOLUTION METHOD

BEZPOŚREDNIE WYZNACZENIE GRANIC MIĘDZYFAZOWYCH γ′ / γ′+γ / γ W UKŁADZIE Ni-Al-Cr NA PODSTAWIE ENTALPII TWORZENIA WYZNACZONYCH KALORYMETRYCZNĄ METODĄ ROZPUSZCZANIA

The work is a continuation of the research carried out on a high-temperature calorimeter solution type on alloys from Ni-Al-Cr system. Thanks to the construction innovation introduced by authors the device allows the determination of the formation enthalpy of alloys at ambient and elevated temperatures. Experiments described in this article were carried out at three temperatures: 873K, 996K and 1150K on the alloys of the chemical compositions from the $Ni_{75}Al_{25}$ ÷ $Ni_{87}Cr_{13}$ section of the Ni-Al-Cr system. On the basis of changes in the enthalpy of formation with increasing chromium content of the alloys, points corresponding to places of phase boundaries γ′ / γ′+γ / γ in Ni-Al-Cr system were determined. A similar relationship was observed in previous studies of alloys from $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$ section. For precise determination of these characteristic points a statistical model was applied

Keywords: solution calorimetry, enthalpy of formation, intermetallic phase, phase boundary

Praca jest kontynuacją badań prowadzonych na skonstruowanym przez autorów wysokotemperaturowym kalorymetrze typu rozpuszczania. Urządzenie pozwala na określanie entalpii tworzenia stopów w podwyższonej temperaturze. Opisywane badania przeprowadzono w trzech temperaturach: 873K, 996K i 1150K na stopach o składach chemicznych znajdujących się na linii $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ układu Ni-Al-Cr. Na podstawie zmian wartości entalpii tworzenia wraz ze wzrostem zawartości chromu w stopach stwierdzono istnienie punktów odpowiadających miejscom występowania granic międzyfazowych γ′ / γ′+γ / γ w układzie Ni-Al-Cr. Podobną zależność zaobserwowano w poprzednich badaniach dotyczących obszaru $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$. Aby precyzyjnie wyznaczyć te charakterystyczne punkty opracowano i zastosowano model statystyczny.

1. Introduction

Ternary Ni-Al-Cr system is crucial for industrial application of nickel-based superalloys and alloys based on intermetallic phase Ni_3Al. Industrial Ni_3Al based alloys with chromium content are two-phase alloys consisting mostly of the ordered phase γ′ and disordered phase γ, contrary to nickel superalloys, where disordered phase γ is a phase dominant over the ordered phase γ′ [1÷6]. Hence, it is important to precisely determine phase boundaries γ′ / γ′+γ / γ in the Ni-Al-Cr system.

Presently one of the widely used method for determination of phase diagrams is CALPHAD procedure [7,8]. A key issue in the case of these method is to provide a reliable experimental data, which are used in the optimization models. The most important data include the enthalpy of formation of alloys. In the case of phase boundaries γ′ / γ′+γ / γ of the Ni-Al-Cr system literature data [9÷11] are based primarily on the studies of samples subjected to rapid cooling e.g. [12,13]. It is connected with difficulties of the research of the changes occurring at elevated temperatures.

Authors of this work considered difficulties connected with keeping the high temperature structure during quenching of the alloys based on Ni_3Al intermetallic phase [14,15], used "in situ" method of direct determination of γ′ / γ′+γ / γ phase boundaries at elevated temperature. For this purpose, specially designed high temperature solution type calorimeter was used [16,17]. Thanks to the construction innovation in the form of intermediate container, allowing for long-term annealing of samples before dropping them into the bath, the device allows the direct determination of the formation enthalpy of alloys at temperatures up to 1400K.

The alloys which chemical compositions belong to the $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ section of Ni-Al-Cr system were examined in this work. As with the previously analyzed by the authors $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$ section [16], location of phase boundaries

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were determined based on the characteristic points of the bends in the course of formation enthalpy values with increasing chromium content. Additionally this time statistical methods were used in order to divide analyzed courses into sections corresponding to the ranges of existing of specific phases and also to precisely determine the points corresponding to places of occurrence of interphase γ′ / γ′+γ and γ′+γ / γ boundaries

2. Preparation of samples and experiment

The research was conducted with use of high temperature calorimeter solution type. Construction of this device as well as operating principle were described in previous works of the authors [16,17].

Alloys studied in this work were made from the metals: Al (99,99%), Ni (99,98%), Cr (99,5%) by casting method. Casting was performed in induction vacuum furnace VSG-02 Balzers, in alundum crucible in vacuum of order 10^{-2} torr. It is worth mentioning that the induction melting and induction heating are commonly used methods for the preparation and processing of alloys including superalloys or alloys based on intermetallic phase Ni_3Al [3,5,13,18÷21]. Alloys were casted into bentonite form, rods of 3mm diameter were obtained. Chemical composition of the samples was analyzed. Aluminum and chromium were analyzed with atomic absorption spectroscopy, the remaining part of the alloy was assumed to be nickel. Table 1 shows results of chemical analysis of samples tested. Subsequently alloys were subjected to heat treatment: alloys were placed in ceramic tubes, that were put in quartz capsules in vacuum. Samples were kept at temperature 1173K for 48h in order to homogenize. Afterwards rapid cooling was conducted in water with ice.

Next, samples placed in intermediate container inside the calorimeter were additionally annealed at temperature of the experiment for a time between 24 and 72 hours . Afterwards, samples were dropped into metallic bath (as a material of the bath, aluminum was used), for dissolving with thermal effect registered by computer. Enthalpy of formation was determined using the equation:

$$\Delta_f H = x_A \Delta H_A^{\phi\cdot} + x_B \Delta H_B^{\phi\cdot} + x_C \Delta H_C^{\phi\cdot} - \Delta H_{A_{x_A}B_{x_B}C_{x_C}}^{\phi\cdot}$$

where: ΔfH – formation enthalpy of the alloy; x_A, x_B, x_C – concentrations (mole fractions) of the alloy components, $\Delta H_A^{\phi\cdot}, \Delta H_B^{\phi\cdot}, \Delta H_C^{\phi\cdot}, \Delta H_{A_{x_A}B_{x_B}C_{x_C}}^{\phi\cdot}$ – heat effects accompanying the dissolution of the components and the alloy in the bath. It is worth mentioning, that thermal effect consists of: heating, melting and solving of the sample in the bath. Enthalpy of formation is determined for temperature, from which sample is dropped into the bath.

TABLE 1

Chemical composition of samples from the $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ section. Component content is given in atomic %.

No.	Component content [atom. %]		Alloy composition
	Cr	Al	
1	0,0	25,0	$Ni_{75,0}Al_{25,0}$
2	1,4	22,4	$Ni_{76,2}Al_{22,4}Cr_{1,4}$
3	2,6	20,0	$Ni_{77,4}Al_{20,0}Cr_{2,6}$
4	3,7	18,0	$Ni_{78,3}Al_{18,0}Cr_{3,7}$
5	5,1	15,1	$Ni_{79,8}Al_{15,1}Cr_{5,1}$
6	6,2	13,2	$Ni_{80,6}Al_{13,2}Cr_{6,2}$
7	7,2	11,0	$Ni8_{1,8}Al_{11,0}Cr_{7,2}$
8	8,0	9,5	$Ni_{82,5}Al_{9,5}Cr_{8,0}$
9	9,4	6,6	$Ni_{84,0}Al_{6,6}Cr_{9,4}$
10	10,4	4,8	$Ni_{84,8}A_{l4,8}Cr_{10,4}$
11	11,5	2,9	$Ni_{85,6}Al_{2,9}Cr_{11,5}$
12	12,4	1,0	$Ni_{86,6}Al_{1,0}Cr_{12,4}$

3. Results

Table 2, 3 and 4 show results of formation enthalpy of the alloys tested at three temperatures: 873K, 996K and 1150K. Results for alloy $Ni_{75,0}Al_{25,0}$ corresponds to stoichiometric phase Ni_3Al. In case of temperature 996K result of formation enthalpy for $Ni_{75,0}Al_{25,0}$ were taken from [16] and for temperatures 873K and 1150K from work of one of the author (K.R.) [22]. Fig. 1, 2 and 3 presents enthalpy of formation of alloys in the function of chromium concentration analyzed with phase boundaries γ′ / γ′+γ / γ indicated on the basis of statistical elaboration.

TABLE 2

Formation enthalpy at temperature 873K of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ obtained by calorimetric solution method.

Alloy composition	Temperature, K	Test no.	Formation enthalpy Δ_fH, kJ/mole of atoms
$Ni_{75,0}Al_{25,0}$ [1)]	873		
		Average	-42,0 ± 1,4 [1)]
$Ni_{76,2}Al_{22,4}Cr_{1,4}$	873	1	-39,9
		2	-40,8
		3	-37,9
		Average	-39,5 ± 1,5
$Ni_{77,4}Al_{20,0}Cr_{2,6}$	873	1	-36,3
		2	-38,5
		3	-37,2
		Average	-37,3 ± 1,1

continuation of TABLE 2

$Ni_{78,3}Al_{18,0}Cr_{3,7}$	873	1	-34,0
		2	-34,9
		3	-32,2
		Average	-33,7 ± 1,4
$Ni_{79,8}Al_{15,1}Cr_{5,1}$	873	1	-28,9
		2	-25,5
		3	-21,3
		Average	-27,3 ± 1,7
$Ni_{80,6}Al_{13,2}Cr_{6,2}$	873	1	-21,4
		2	-24,1
		3	-21,3
		Average	-22,3 ± 1,6
$Ni_{81,8}Al_{11,0}Cr_{7,2}$	873	1	-16,5
		2	-16,8
		3	-19,4
		Average	-17,6 ± 1,6
$Ni_{82,5}Al_{9,5}Cr_{8,0}$	873	1	-13,8
		2	-15,3
		3	-14,9
		Average	-14,7 ± 0,8
$Ni_{84,0}Al_{6,6}Cr_{9,4}$	873	1	-10,6
		2	-7,3
		3	-9,4
		Average	-9,1 ± 1,7
$Ni_{84,8}Al_{4,8}Cr_{10,4}$	873	1	-6,3
		2	-5,6
		3	-4,0
		Average	-5,3 ± 1,2
$Ni_{85,6}Al_{2,9}Cr_{11,5}$	873	1	-5,8
		2	-4,6
		3	-4,1
		Average	-4,8 ± 0,9
$Ni_{86,6}Al_{1,0}Cr_{12,4}$	873	1	-3,9
		2	-3,8
		3	-5,9
		Average	-4,5 ± 1,2

[1)] Data from work [22].

TABLE 3

Formation enthalpy at temperature 996K of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ obtained by calorimetric solution method.

Alloy composition	Temperature, K	Test no.	Formation enthalpy Δ_fH, kJ/mole of atoms
$Ni_{75,0}Al_{25,0}$[1)]	996	1	-41,5
		2	-39,8
		3	-41,0
		4	-42,7
		Average	-41,8 ± 0,9
$_{Ni}76,2Al_{22,4}Cr_{1,4}$	996	1	-40,0
		2	-41,2
		3	-38,3
		4	-39,5
		Average	-39,8 ± 1,2

continuation of TABLE 3

$Ni_{77,4}Al_{20,0}Cr_{2,6}$	996	1	-37,4
		2	-35,9
		3	-34,3
		Average	-35,8 ± 1,5
$Ni_{78,3}Al_{18,0}Cr_{3,7}$	996	1	-30,4
		2	-31,7
		3	-33,5
		Average	-31,8 ± 1,5
$Ni_{79,8}Al_{15,1}Cr_{5,1}$	996	1	-27,5
		2	-26,9
		3	-24,2
		Average	-26,2 ± 1,7
$Ni_{80,6}Al_{13,2}Cr_{6,2}$	996	1	-22,7
		2	-19,3
		3	-21,2
		Average	-21,1 ± 1,7
$Ni_{81,8}Al_{11,0}Cr_{7,2}$	996	1	-18,5
		2	-17,4
		3	-15,9
		Average	-17,2 ± 1,3
$Ni_{82,5}Al_{9,5}Cr_{8,0}$	996	1	-12,4
		2	-12,6
		3	-14,8
		Average	-13,3 ± 1,3
$Ni_{84,0}Al_{6,6}Cr_{9,4}$	996	1	-8,4
		2	-7,2
		3	-6,1
		Average	-7,2 ± 1,1
$Ni_{84,8}Al_{4,8}Cr_{10,4}$	996	1	-7,9
		2	-5,9
		3	-5,5
		Average	-6,4 ± 1,3
$Ni_{85,6}Al_{2,9}Cr_{11,5}$	996	1	-3,6
		2	-5,0
		3	-6,3
		Average	-4,9 ± 1,3
$Ni_{86,6}Al_{1,0}Cr_{12,4}$	996	1	-5,5
		2	-3,6
		3	-4,0
		Average	-4,4 ± 1,0

[1)] Data from work [16].

TABLE 4

Formation enthalpy at temperature 1150K of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ obtained by calorimetric solution method.

Alloy composition	Temperature, K	Test no.	Formation enthalpy Δ_fH, kJ/mole of atoms
$Ni_{75,0}Al_{25,0}$[1)]	1150		
		Average	-42,3 ± 1,6[1)]
$Ni_{76,2}Al_{22,4}Cr_{1,4}$	1150	1	-38,3
		2	-39,8
		3	-41,3
		Average	-39,8 ± 1,5

continuation of TABLE 4			
$Ni_{77,4}Al_{20,0}Cr_{2,6}$	1150	1	-32,3
		2	-33,4
		3	-34,9
		Average	-33,5 ± 1,3
$Ni_{78,3}Al_{18,0}Cr_{3,7}$	1150	1	-27,4
		2	-28,6
		3	-30,8
		Average	-28,9 ± 1,8
$Ni_{79,8}Al_{15,1}Cr_{5,1}$	1150	1	-23,7
		2	-23,7
		3	-20,8
		Average	-22,7 ± 1,7
$Ni_{80,6}Al_{13,2}Cr_{6,2}$	1150	1	-16,7
		2	-16,9
		3	-18,7
		Average	-17,4 ± 1,1
$Ni_{81,8}Al_{11,0}Cr_{7,2}$	1150	1	-14,1
		2	-12,2
		3	-13,4
		Average	-13,2 ± 1,0
$Ni_{82,5}Al_{9,5}Cr_{8,0}$	1150	1	-10,6
		2	-7,3
		3	-8,8
		Average	-8,9 ± 1,7
$Ni_{84,0}Al_{6,6}Cr_{9,4}$	1150	1	-8,9
		2	-7,1
		3	-6,3
		Average	-7,3 ± 1,5
$Ni_{84,8}Al_{4,8}Cr_{10,4}$	1150	1	-4,6
		2	-7,2
		3	-6,3
		Average	-6,0 ± 1,3
$Ni_{85,6}Al_{2,9}Cr_{11,5}$	1150	1	-3,8
		2	-6,5
		3	-5,8
		Average	-5,4 ± 1,4
$Ni_{86,6}Al_{1,0}Cr_{12,4}$	1150	1	-5,6
		2	-4,8
		3	-3,4
		Average	-4,6 ± 1,2

[1)] Data from work [22].

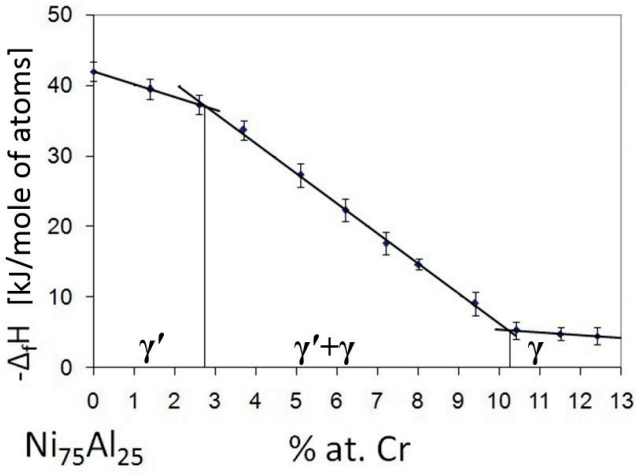

Fig. 1. Course of formation enthalpy of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ with indicated γ′ / γ′+γ / γ phase boundaries (873K)

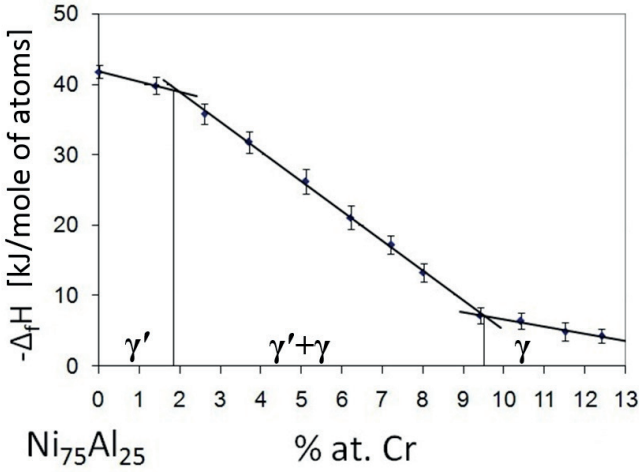

Fig. 2. Course of formation enthalpy of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ with indicated γ′ / γ′+γ / γ phase boundaries (996K)

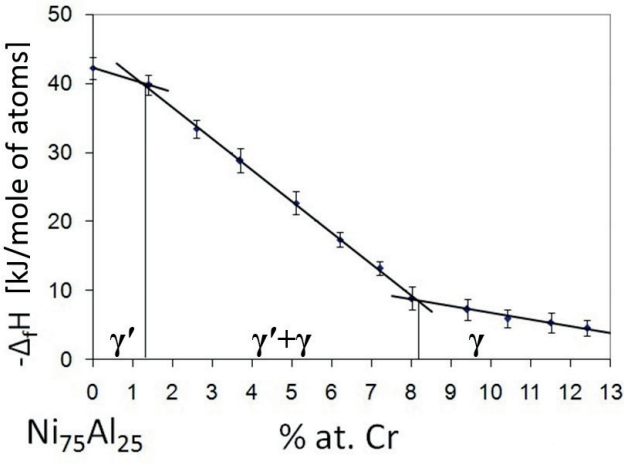

Fig. 3. Course of formation enthalpy of alloys from section $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ with indicated γ′ / γ′+γ / γ phase boundaries (1150K)

TABLE 5

Results of statistical analysis showing places of γ′ / γ′+γ and γ′+γ / γ phase boundaries in alloys from range $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ from Ni-Al-Cr system – calorimetric method solution type

$Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$	873K		996K		1150K	
	γ′ / γ′+γ	γ′+γ / γ	γ′ / γ′+γ	γ′+γ / γ	γ′ / γ′+γ	γ′+γ / γ
% at. Cr	**2,73**	**10,25**	**1,82**	**9,53**	**1,38**	**8,17**
Standard error	0,44	0,76	0,42	0,31	0,30	0,24
-95% confidence level	1,56	9,65	1,03	8,85	0,79	7,79
+95% confidence level	4,04	11,15	3,56	10,27	2,04	8,79

4. Direct determination of γ′ / γ′+γ / γ phase boundaries

In all cases analyzed, presented in Tables 2÷4 it can be seen the drop of absolute value of the enthalpy formation with increasing concentration of chromium. This is due to the increasing contribution of disordered γ phase in the alloy, which occurs with the addition of chromium. It should be emphasized that the disordered γ phase is the phase of higher energy than the ordered phase γ′. A consequence is, that lower input of energy is necessary for breaking the bonding between of atoms during solution in the case of disordered g phase and this fact is reflected on the higher formation enthalpy value of g phase. Just as was the case in studies of alloys of the $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$ section [16], formation enthalpy changes take place in stages. It allows dividing tested range into sections corresponding to the ranges of occurrence of the phases and gives the possibility to directly determine phase boundaries γ ′/ γ′+γ / γ.

Statistical methods were used (previously they were applied for studies of Ni_3Al÷Ni_3Fe alloys [23]) to divide formation enthalpy course into sections. Program Statistica from Statsoft company was used for computing. The first step was to create a model function describing the analyzed courses. In the case of three-segment model it was:

$$\Delta_f H = A_1 \times \%\text{ at. Cr} + B_1 \quad \text{for} \quad \%\text{ at. Cr} < P_1$$
$$\Delta_f H = A_2 \times \%\text{ at. Cr} + B_2 \quad \text{for} \quad P_1 \le \%\text{ at. Cr} < P_2$$
$$\Delta_f H = A_3 \times \%\text{ at. Cr} + B_3 \quad \text{for} \quad \%\text{ at. Cr} \ge P_2$$

where:
$\Delta_f H$ – formation enthalpy,
A_i, (i = 1, 2, 3) – slope of a straight line of segment analyzed,
B_i, (i = 1, 2, 3) – point ordinate, segment analyzed is located on straight line which crosses axes of ordinates,
% at. Cr – alloying additive content (chromium) in at. %,
P_1 – intersection point corresponding to phase boundary γ′ / γ′+γ
P_2 – intersection point corresponding to phase boundary γ′+γ / γ

For function as a:

$$\Delta_f H = (\%\text{ at. Cr} < P_1) \times (A_1 \times \%\text{ at. Cr} + B_1) + (P_1 \le \%\text{ at. Cr} < P_2) \times (A_2 \times \%\text{ at. Cr} + B_2) + (\%\text{ at. Cr} \ge P_2) \times (A_3 \times \%\text{ at. Cr} + B3)$$

basing on minimization of the sum of square deviation parameters of the model were determined, estimating the location of boundary points. Subsequently for boundary values of sections, linear regression analysis was carried out, as a result coefficient and constants of the linear regression and their statistical significance were obtained. The points of intersections of segments with their standard deviations were also determined.

In addition to the directional coefficients of adjacent sections, the test of equality of regression coefficients was carried out. For the verification of the hypotheses assumed p-value = 0.05, which corresponds to a probability of error equal to 5%. Statistical significance of regression coefficients, which form the ground to justify the division of the formation enthalpy course into sections were achieved as the test result.

In table 5 results of statistical analysis of the points corresponding to places of occurrence phase boundaries for alloys from the intersection line: $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ from Ni-Al-Cr system are presented. Their graphical interpretation is shown in figures 1 to 3.

5. Conclusions

1. Alloys from $Ni_{75}Al_{25}$÷$Ni_{87}Cr_{13}$ section of Ni-Al-Cr system were used for research by calorimetric solution method. Thanks to introduction an intermediate container into the calorimeter which was a novel construction innovation proposed by authors, it was possible to determine enthalpy of formation at elevated temperature. In this work enthalpy of formation was determined at three temperatures: 873K, 996K and 1150K.
2. Obtained results of enthalpy of formation showed the decrease of its absolute value with increasing chromium content in tested alloys. It refers to all three temperatures. This tendency was also stated in previous calorimetric research for alloys from $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$ section.
3. For alloys analyzed in this work as well as in previously studied at the same temperatures $Ni_{75}Al_{25}$÷$Ni_{75}Cr_{25}$ alloys there are visible characteristic bend points of course of formation enthalpy as a function of chromium concentration.
4. Points referring to bends of course of formation enthalpy values as a function of chromium concentration are attributed to phase boundaries γ′ / γ′+γ and γ′+γ / γ.
5. Statistical model was applied which enabled for precise determination places of γ′ / γ′+γ / γ phase boundaries

basing on obtained courses of enthalpy of formation. It was used for results obtained for alloys studied in this work.

6. Applied calorimetric "in situ" method is a valuable tool for high-temperature alloy research not only because it provides thermodynamic data of enthalpy of formation (valuable e.g. from the point of view of CALPHAD method), but also show possibility of direct determination of phase boundaries based on its course.

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